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Comparative electrochemistry of phenothiazine dyes incorporated into Nafion and poly(styrenesulfonate) films

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Abstract. The electrochemical properties of phenothiazine dyes, thionine (TH^+) and methylene blue (MB^+), incorporated into Nafion and PSS films were studied. These dyes showed different electrochemical behaviour in Nafion film when compared to aqueous solution and PSS film. The observed electrochemical behaviour has been explained by the interaction of reduced TH^+ and MB^+ molecules with different regions of the Nafion film. In the PSS film, the incorporated dye molecules experienced purely a hydrophilic environment and showed electrochemical properties similar to that of aqueous solution. Further, the interaction of the reduced MB^+ molecules with the hydrophobic fluorocarbon region of the Nafion film was studied by spectroelectrochemistry adding 2-propanol to the supporting electrolyte solution.

Keywords. Electrochemistry; spectroelectrochemistry; phenothiazine dyes; Nafion; poly(styrenesulfonate).

1. Introduction

Nafion, a perfluorosulfonate ion-exchange polymer (figure 1a), continues to be the most studied ion-exchange polymer in modified electrodes [1-5]. The electroactive and photoactive molecules incorporated into Nafion film found applications in the field of electrocatalysis, electrochromic devices and biosensors [1,6-10]. The cluster-like morphology of Nafion film has been considered analogous with that of reversed micelles [11]. It is an excellent polymer to study the effects of electrostatic and hydrophobic interactions. On the other hand, the other ion-exchange polymer, poly(styrenesulfonate), PSS, (figure 1b) has quite a different film structure and imposes a different microenvironment [12] on the incorporated molecules when compared to Nafion film. The structure of PSS film is essentially homogeneous because of the uniform distribution of the charged sites along the polymer chains [12] whereas the structure of the Nafion film consists of hydrophilic sulfonate ionic cluster, fluorocarbon hydrophobic regions and the interfacial regions formed between these two [11].

Dye modified electrodes have been studied extensively in relation to many potential applications [13-18]. In order to understand the interaction of these dye molecules with ionic polymer films, we have studied the electrochemical properties of these dyes incorporated into PSS film and compared the results with those obtained in Nafion film.

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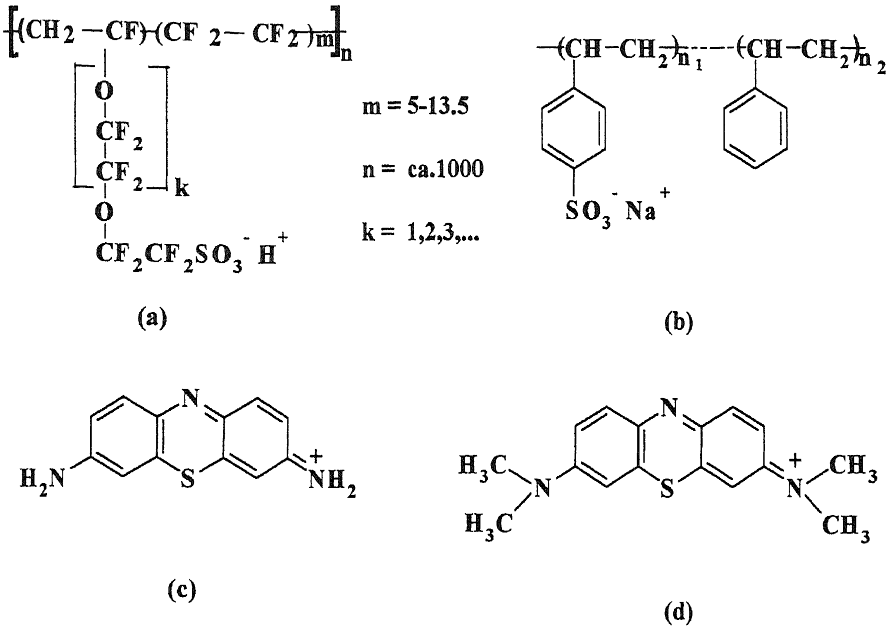

Figure 1. (**a**) Nafion polymer, (**b**) Poly(styrenesulfonate)polymer, (**c**) thionine and (**d**) methylene blue.

2. Experimental

A 5% Nafion solution (Aldrich, EW 1100, dissolved in lower aliphatic alcohol and water) was diluted to 1% with ethanol. Polystyrene (PS) was obtained from Aldrich and used as received. The phenothiazine dyes, TH$^+$ and MB$^+$ (Aldrich), (figures 1c and 1d) were purified by chromatographic method [19-20]. All other chemicals were of analytical grade and used without further purification. The platinum (Pt) plate electrodes were pretreated by using the standard procedures [21]. For electrochemical experiments, the Nafion film coating on the Pt electrode was prepared by casting 9 µl of 1% Nafion solution onto a 1 cm^2 Pt electrode and dried at room temperature followed by keeping the Nafion-coated electrode in distilled water for 30 min (represented as Pt/Nf). The thickness of the Nafion film was calculated as 0·56 µm using a density of 1·58 g/cm^3 for wet Nafion film [22]. PSS film on the Pt electrode was prepared [23] by casting a known volume of 10% solution of PS in toluene on a 1 cm^2 Pt electrode and dried at room temperature. Then the PS film was chlorosulfonated with a 4% solution of chlorosulfonic acid in 1,2-dichloroethane for 3 min. After this treatment, the electrode was rinsed with 1,2-dichloroethane to remove the chlorosulfonic acid in the polymer coating. For the formation of sulfonated groups the electrode was soaked in KCl solution for 1h (represented as Pt/PSS). The thickness of the resultant PSS film was 3 µm [12,23]. The Nf and PSS films were highly stable on the electrode surface and did not detach from the electrode surface under immersion in electrolyte solution. The Pt/Nf or Pt/PSS electrode was dipped in a known concentration of dye solution, and then washed with distilled water and used for electrochemical experiments (represented as Pt/Nf/dye and Pt/PSS/dye).

A three-electrode cell was used with Pt/Nf/dye or Pt/PSS/dye as working electrode, 1 cm^2 Pt plate as counter electrode and a saturated calomel electrode (SCE) as reference. Cyclic voltammograms were recorded on an EG&G PAR 273A potentiostat/galvanostat equipped with RE0151 recorder. Potentials were measured and quoted with respect to SCE. The amount of electroactive species was determined by the chronocoulometry method [24]. The electrochemical cell solutions were purged with nitrogen for 30 min before each experiment. For spectroelectrochemical studies, 1% Nafion solution was coated on a 1 cm^2 ITO (Indium Tin Oxide) plate and dried at room temperature and then dipped in distilled water for 30 min. The Nafion coated ITO electrode was dipped in dye solution for 3–5 min and then the electrode was washed with distilled water before use (represented as ITO/Nf/dye). The absorption spectra were recorded *in situ* using an Otsuka Electronics IMUC-7000 diode array multichannel detection system.

3. Results and discussion

3.1 *Electrochemistry of TH^+ and MB^+ in Nafion and PSS films*

The dye molecules undergo a two-electron redox process [25,26] and the anodic peak current i_{pa} was found to be lower than the cathodic peak (i_{pc}) in 0·5 M H_2SO_4. The observed lower i_{pa} has been explained by the formation of dimer dye molecules during the oxidation process in solution [25]. Figure 2 shows the cyclic voltammograms recorded at different scan rates for Pt/Nf/TH^+ and Pt/PSS/TH^+ electrodes dipped in 0·5 M H_2SO_4. The electrochemical data obtained for TH^+ and MB^+ in Nafion and PSS films are summarised in table 1. At a scan rate of 50 mV/s, TH^+ in Nafion film showed a small negative shift in the cathodic peak potential and the i_{pa} value was higher than the i_{pc} value (figure 2A) when compared to TH^+ in aqueous acidic solution. However, TH^+ showed an E_{pc} value of 0·21 V and the i_{pa} value was slightly lower than the i_{pc} value in PSS film (figure 2B) which is very similar to that of TH^+ in aqueous acidic solution[26]. The cyclic voltammograms recorded for Pt/Nf/MB^+ and Pt/PSS/MB^+ electrodes dipped in 0·5 M H_2SO_4 at different scan rates are shown in figure 3. MB^+ in Nafion film showed a 40 mV negative shift in E_{pc} value (0·16 V) and a peak separation (ΔEp) of 90 mV (figure 3A) when compared to MB^+ in PSS film ($E_{pc} = 0{\cdot}20$ V and $\Delta Ep = 30$ mV) (figure 3B) at a scan rate of 50 mV/s. The plots of peak current against the square root of scan rates for TH^+ and MB^+ in Nafion and PSS films are shown in figure 4. TH^+ in Nafion film showed higher slope for i_{pa} than i_{pc}. It was the reverse in the case of TH^+ in PSS film. In the case of MB^+, even though the trend observed for i_{pa} and i_{pc} was the same in Nafion and PSS films, only a small difference in the slopes of i_{pc} and i_{pa} was observed for MB^+ in PSS film when compared to Nafion film (figure 4).

The earlier studies have shown that the molecules interacting with the hydrophobic region of the Nafion film showed a negative shift in the E_{pc} value [27]. In the present investigation, TH^+ showed only a small negative shift in the E_{pc} value in Nafion film (table 1). This observation indicates that the interaction between TH^+ and the hydrophobic region of the Nafion film is not significant. The incorporated TH^+ molecules mostly occupies the ionic cluster and interfacial regions of the Nafion film. The observed higher i_{pa} value for TH^+ in Nafion film showed that the reduced form of TH^+ (TH_3^+) interacted with the hydrophilic ionic cluster region of the Nafion film when

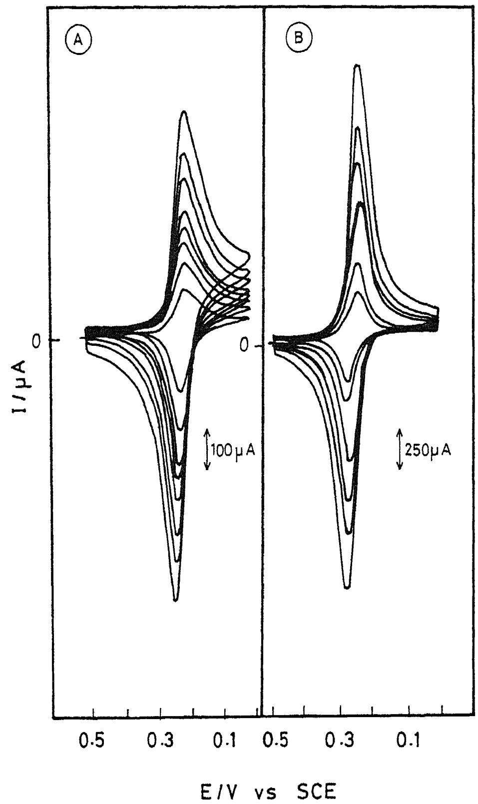

Figure 2. Cyclic voltammograms recorded for (**A**) Pt/Nf/TH$^+$ and (**B**) Pt/PSS/TH$^+$ in 0·5 M H_2SO_4.
Scan rates: (**A**) = 5, 10, 20, 30, 40, 50, 75 and 100 mV/s and (**B**) = 5, 10, 20, 50, 75 and 100 mV/s.

Table 1. Electrochemical data of TH$^+$ and MB$^+$ in Nafion and PSS films*

Film	Dye	E_{pc}, mV	ΔE_p, mV	i_{pc}/i_{pa}
Nafion	TH$^+$	190	40	1·42
	MB$^+$	160	90	0·68
PSS	TH$^+$	210	30	0·93
	MB$^+$	200	30	0·90

*Scan rate = 50 mV/s and H_2SO_4 = 0.5 M

compared to TH$^+$. The observed negative shift in the E_{pc}, lower i_{pa} and large ΔE_p values for MB$^+$ in Nafion film were due to the stronger interaction of the reduced MB$^+$ with the hydrophobic and interfacial regions of the Nafion film [17]. However, in PSS film, MB$^+$ experienced a hydrophilic environment and showed electrochemical behaviour very similar to that of TH$^+$ in aqueous acidic solution. The electrochemistry of

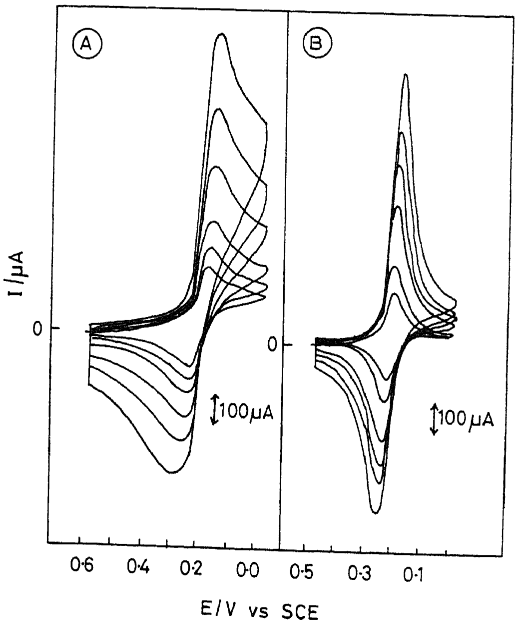

Figure 3. Cyclic voltammograms recorded for (**A**) Pt/Nf/MB^+ and (**B**) Pt/PSS/MB^+ in 0·5 M H_2SO_4. Scan rates: (**A**) and (**B**) = 10, 20, 50, 75, 100 and 150 mV/s.

$[Os(bpy)_3]^{2+}$ complex in PSS film has been reported [28] and it was found that the $[Os(bpy)_3]^{3+}$ is more strongly attached to PSS film than that of $[Os(bpy)_3]^{2+}$ and that the electrostatic interaction affect the ion-exchange equilibria more than the hydrophobic interaction. Similarly, TH^+ and MB^+ are also strongly attached to the PSS film by electrostatic interaction rather than hydrophobic interaction and showed electrochemical behaviour similar to that of TH^+ and MB^+ in aqueous solution. However, in Nafion film, the situation was quite different and the hydrophobic interaction was predominant and promoted a stronger hydrophobic binding between the Nafion film and the less charged molecules. The reduced MB^+ (MBH_2^+) was less charged and interacted strongly with the hydrophobic regions of the Nafion film which resulted in a negative shift in the E_{pc}, lower i_{pc} than that i_{pa} and higher ΔE_p.

3.2 *Effect of 2-propanol on the electrochemistry of MB^+ in Nafion film*

In Nafion film, the molecules residing in the hydrophobic region are electrochemically inactive whereas the molecules residing in the ionic cluster and interfacial regions of the Nafion film are electrochemically active [29]. It has been reported that the electroinactive molecules in the Nafion film became electroactive upon the addition of 2-propanol to the supporting electrolyte solution [29]. The chronocoulometry experiments showed that all the incorporated TH^+ molecules in the Nafion film were electrochemically active whereas part of the incorporated MB^+ molecules were electrochemically inactive. This result showed that the TH^+ molecules were incorporated into the electroactive region of the Nafion film while part of the MB^+ molecules occupied the hydrophobic region of the Nafion film. In the case of PSS film, all the incorporated

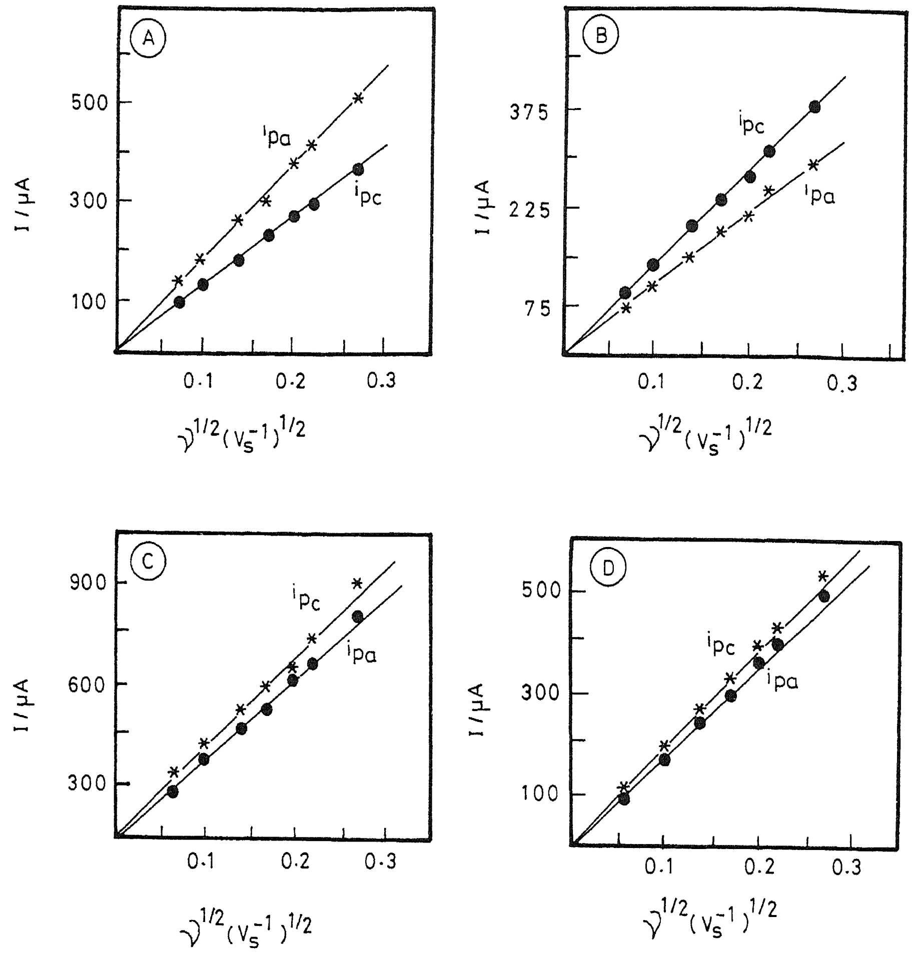

Figure 4. Plots of peak currents against squareroot of scan rates. (**A**) Pt/Nf/TH^+, (**B**) Pt/Nf/MB^+, (**C**) Pt/PSS/TH^+ and (**D**) Pt/PSS/MB^+.

TH^+ and MB^+ molecules were electrochemically active. The cyclic voltammograms recorded for Pt/Nf/MB^+ electrode in 0·5 M H_2SO_4 and in a mixture of 0·5 M H_2SO_4 and 0·8 M 2-propanol are shown in figure 5. The electrochemical data obtained for MB^+ in Nafion film upon the addition of different concentrations of 2-propanol are summarised in table 2. Upon the addition of 0·8 M 2-propanol to 0·5 M H_2SO_4, the E_{pc} value was shifted positively by 50 mV, the peak separation decreased from 90 to 50 mV and the peak currents and the amount of electroactive species (Γ) increased nearly twofold. The observed behaviour clearly showed that part of the incorporated MB^+ molecules interacted strongly with the hydrophobic region of the Nafion film in the absence of 2-propanol. Upon the addition of 2-propanol, the 2-propanol entered into the Nafion film and the film swelled very well. In a swelled Nafion film, the MB^+ molecules slowly migrated from the electroinactive hydrophobic region to the electroactive regions of the Nafion film and showed higher electrochemical activity. When the same electrode was transferred into 0·5 M H_2SO_4, the electrochemical activity was

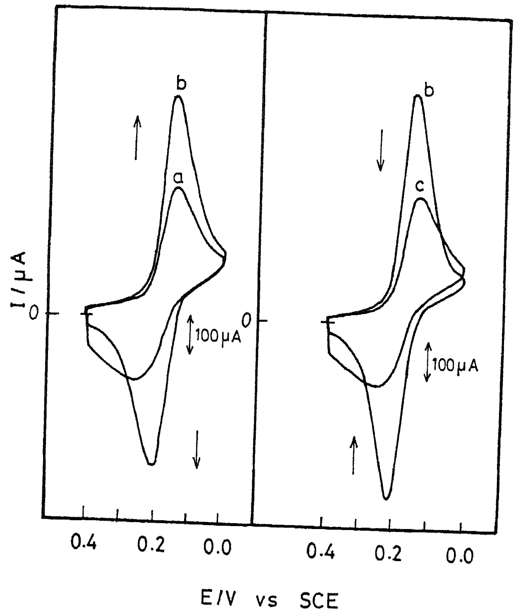

Figure 5. Cyclic voltammograms recorded for Pt/Nf/MB$^+$ in (a) 0·5 M H_2SO_4, (b) 0·5 M H_2SO_4 and 0·8 M 2-propanol and (c) as in (a). Scan rate = 50 mV/s.

Table 2. Electrochemical data of MB$^+$ incorporated into Nafion film upon the addition of different concentrations of 2-propanol in 0·5 M $H_2SO_4^*$

[2-propanol], M	Γ, 109, mol cm^{-2}	E_{pc} mV	ΔE_p mV	i_{pc} μA
0·0	2·5	160	90	280
0·2	3·6	180	70	400
0·4	4·1	190	60	460
0·6	4·4	200	50	500
0·8	4·9	210	50	540

*Scan rate = 50 mV/s.

decreased and a negative shift in the E_{pc} value with a large peak separation was observed (figure 5c). Similar increase in the peak currents were not observed for TH$^+$ in Nafion film upon the addition of 2-propanol. This showed that the TH$^+$ molecules mainly occupied the electroactive regions of the Nafion film in the absence of 2-propanol. In the case of TH$^+$ and MB$^+$ in PSS film, the addition of 2-propanol decreased the peak currents due to the leaching of both TH$^+$ and MB$^+$ molecules from the PSS film.

3.3 *Spectroelectrochemical studies of TH$^+$ and MB$^+$ in Nafion film*

The interaction of reduced TH$^+$ and MB$^+$ molecules with hydrophilic and hydrophobic regions of the Nafion film is also understood from the spectroelectrochemical

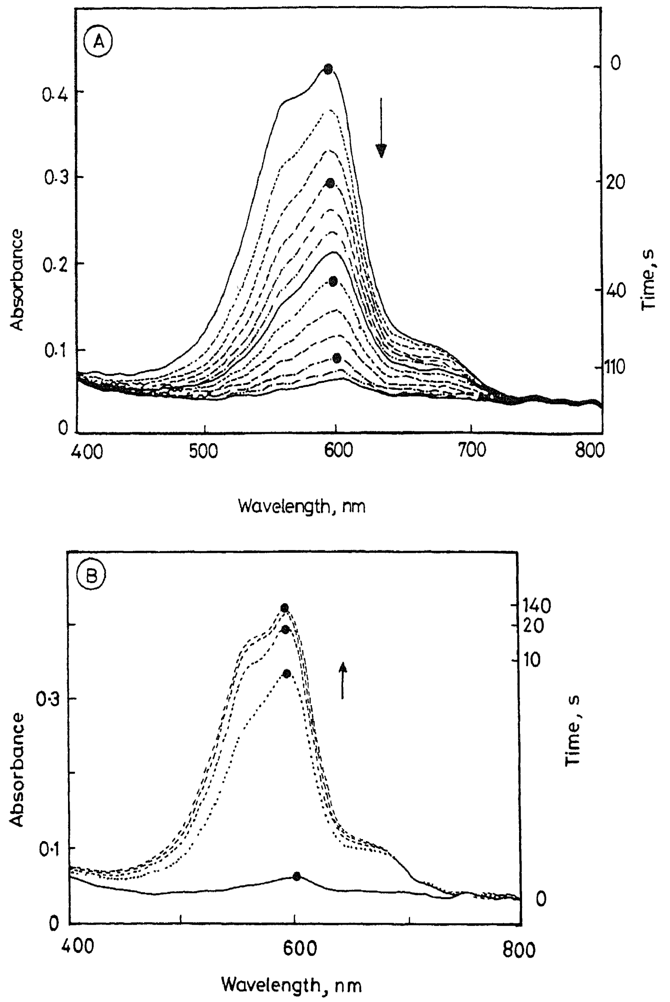

Figure 6. Absorption spectral changes observed *in situ* for ITO/Nf/TH$^+$ electrode dipped in 0·5 M H_2SO_4 at applied potentials of (**A**) and (**B**) 0·6 V.

studies. The absorption spectral changes recorded for ITO/Nf/TH$^+$ electrode dipped in 0·5 M H_2SO_4 at applied potentials of 0 and 0·6 V are shown in figure 6. The absorption spectrum initially showed a main band due to monomer TH$^+$ at 600 nm and two shoulder bands due to dimer and protonated TH$^+$ molecules at 555 and 675 nm respectively. At an applied potential of 0 V, the absorption spectrum almost disappeared due to the reduction of TH$^+$. The complete reduction of TH$^+$ occurred in about 160 sec (figure 6A). When a potential of 0·6 V was applied to the same electrode, the original absorption spectrum reappeared within 140 sec (figure 6B). The results showed that the time taken for the oxidation and reduction of TH$^+$ in Nafion was almost the same.

The absorption spectral changes recorded for ITO/Nf/MB$^+$ electrode dipped in 0·5 M H_2SO_4 at applied potentials of 0 and 0·6 V are shown in figure 7. Before applying a potential of 0 V, MB$^+$ showed a main band due to monomer MB$^+$ at 660 nm and two

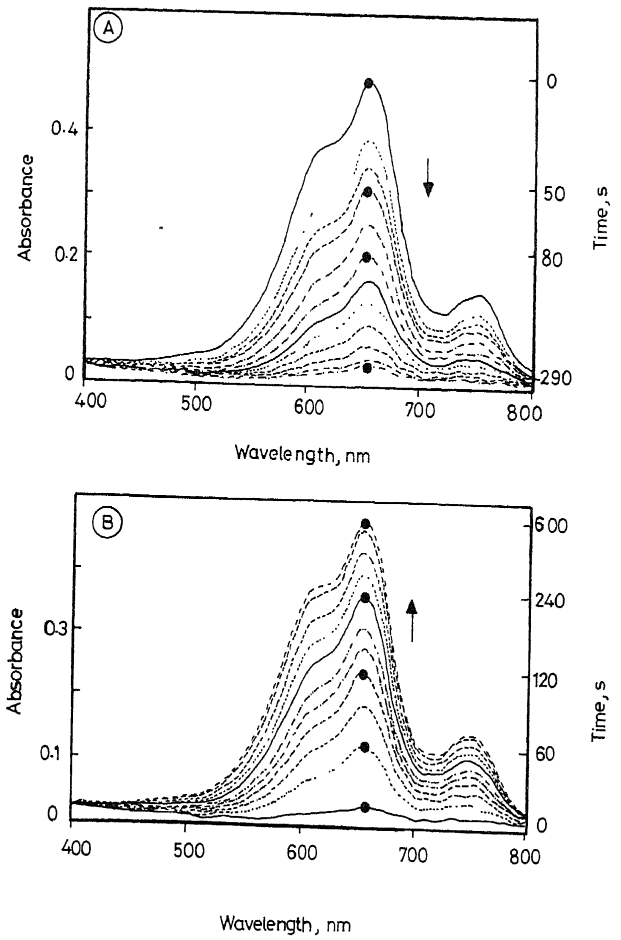

Figure 7. Absorption spectral changes observed *in situ* for ITO/Nf/MB$^+$ electrode dipped in 0·5 M H_2SO_4 at applied potentials of (**A**) 0 and (**B**) 0·6 V.

shoulder bands due to dimer and protonated MB$^+$ molecules at 600 and 770 nm respectively. At an applied potential of 0 V, the absorption bands due to monomer, dimer and protonated MB$^+$ completely disappeared after 300 sec (figure 7A). When a potential of 0·6 V was applied to the same electrode, the oxidation of reduced MB$^+$ occurred in about 600 sec (figure 7B). The observed behaviour clearly showed that the reduction of MB$^+$ in Nafion film was faster than the oxidation of reduced MB$^+$. Even at lower concentration of MB$^+$ in Nafion film, the oxidation of reduced MB$^+$ took a longer time than the reduction of MB$^+$. This was mainly due to the stronger interaction of reduced MB$^+$ with the hydrophobic regions of the Nafion film. On the other hand, the reduced TH$^+$ mostly interacted with the hydrophilic regions of the Nafion film where TH$^+$ underwent reduction and oxidation at a relatively faster time scale.

3.4 *Stability of MB$^+$ in Nafion and PSS films*

The hydrophobic interaction of MB$^+$ molecules with the Nafion film was also studied by the stability of the two-electron reduced (MBH_2^+) molecule in the Nafion film.

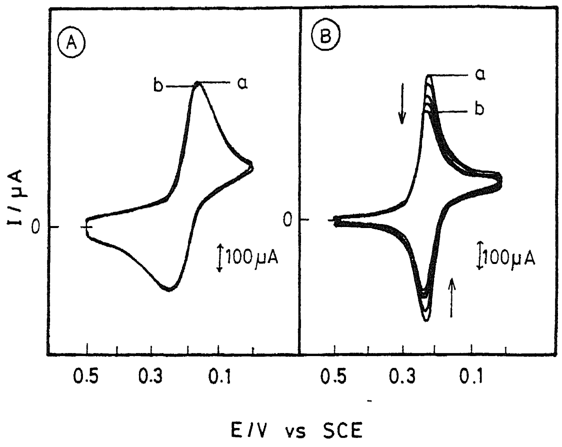

Figure 8. Cyclic voltammograms recorded for (A) Pt/Nf/MB$^+$ and (B) Pt/PSS/MB$^+$ at different time intervals in 0·5 M H_2SO_4. (a) 0 min and (b) after 15 min.

The cyclic voltammograms recorded for MB$^+$ in Nafion and PSS films at different time intervals are shown in figure 8. The cyclic voltammograms of MB$^+$ in PSS film slowly decreased at regular time intervals (figure 8B). However, the cyclic voltammograms of MB$^+$ in Nafion film did not decrease even after 15 min (figure 8A). The observed behaviour showed that the reduced MB$^+$ molecules (MBH$_2^+$) was strongly held in the interfacial region of the Nafion film and showed higher stability. In PSS film, such an interaction was not present and hence the cyclic voltammograms decreased due to slow leaching of MB$^+$ upon cycling at different time. A slow decrease in the peak currents was observed for TH$^+$ in Nafion film due to the leaching of TH$^+$ from the Nafion film. This is due to the weak interaction of the two-electron reduced TH$^+$ (TH$_3^+$) molecules with the Nafion film. On the other hand, a marginal decrease in the peak currents was observed for TH$^+$ in PSS film and the cyclic voltammogram almost disappeared after 15 min due to the complete leaching of TH$^+$ from the PSS film. Among the two dyes, MB$^+$ is more hydrophobic than the TH$^+$ and interacts strongly with the hydrophobic region of the Nafion film and showed higher stability upon repeated cycles or when it was immersed in 0·5 M H_2SO_4 for several hours.

The electrochemical behaviour of TH$^+$ and MB$^+$ in PSS film was also studied at lower acid concentration of 0·05 M H_2SO_4. Both the dyes showed a very similar electrochemical behaviour as observed in 0·5 M H_2SO_4. On the other hand, both TH$^+$ and MB$^+$ in 0·05 M H_2SO_4 exhibited an unusual redox wave at more positive potential in addition to the usual redox wave at least positive potential which has been explained by the interaction of these dyes with different regions of the Nafion film (16). In homogeneous solution, the change of acid concentration in the range between 0·05 to 0·5 M H_2SO_4 does not affect the electrochemical behaviour of the TH$^+$ and MB$^+$ dyes.

Conclusion

The electrochemical behaviour of MB$^+$ and TH$^+$ in Nafion film shows quite different electrochemical properties when compared to PSS film. The electrochemical behaviour exhibited by the dye molecules in the PSS film are very similar to that of dyes in aqueous solution. The swelling factors (ratios of wet to dry thicknesses) of PSS and Nafion films in aqueous medium are ≈ 14 and ≈ 2·3 respectively[12] which implies that substantially more water is present in the pores of the PSS film. Thus, ion-solvation in the PSS film is similar to that of aqueous solution but quite a different ionic surrounding is encountered in the Nafion film depending on whether the incorporated molecules reside in the water-rich ionic clusters or in the water-poor interfacial and hydrophobic fluorocarbon zones. The polar head group (SO_3^-) is attached at the end of a long side chain originating from the fluorocarbon backbone in the Nafion polymer. In the PSS film, the polar head group (SO_3^-) is near to the hydrocarbon chain of the PSS polymer. The long side chain in the Nafion polymer separates the hydrophobic flurocarbon and hydrophilic ionic cluster regions. Such a situation does not exist in the PSS film which reduces the volume of the hydrophobic and interfacial regions in the PSS film. Due to the weak hydrophobic interaction, the dye molecules are not held tightly in the PSS films when compared to the Nafion film. Further, the interaction of these dye molecules with different regions of the Nafion film was supported by the spectroelectrochemical studies. Thus the different film morphology and ion-solvation are the reasons for the different electrochemical behaviour observed for the TH^+ and MB^+ molecules in the Nafion and PSS films.

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